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BATCH ADSORPTION OF PHENOL FROM INDUSTRIAL WASTE WATER USING CEREAL BY-PRODUCTS AS A NEW ADSRBENT

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Abstract

Phenol is an important chemical which is used in the manufacture of many products such as dyes, synthetic resins, pesticides, tanning materials, perfumes and medicinal products, lubricants, essential oils, solvents, etc. It is very toxic even present as traces in industrial wastewater effluents. It may constitute a potential pollution source of ground waters and hence it has to be eliminated.

In the work the elimination of phenol from synthesized aqueous solutions was carried out by adsorption onto non activated carbon obtained from calcinations up to 600°C in exclusion air of a local cereal by-product.

A kinetic study was also included where equilibrium was reached at the end of 120 minutes. A parametric study was also performed by investigating the effect of key parameters such as the pH and initial concentration. The adsorption isotherm was also examined where the results showed that at low concentrations, it is of type IV according to the BET classification whereas at high values of concentration the process seemed to be of a multi-layer type.

The results showed that a high retention of the phenol exceeding 70% was achieved for an initial concentration of 20 mg/l, at 20°C, a mean size diameter of 0.1 mm, a mixing velocity of 600 rpm, an adsorbent concentration of 10 g /l, a pH=3 and contact time of two hours

Key words: industrial waste water, phenol, organic pollutant, adsorption, elimination, natural adsorbent.

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1. Introduction

Phenolic compounds are considered to be hazardous wastes, which are released into aquatic environment by industries such as pharmaceutical, chemical, petroleum refineries, phenolic resin, fertilizer, It is well known that the contamination of the water, from the industries provides many problems to human's health including diarrhea, liver damage, anaemia and dark urin [1]. Especially, phenols are considered as priority pollutants since they are harmful to organisms at lox concentrations and cause significant taste and odour problems to drinking water [2].

The treatment processes for phenolic wastewater can be classified into two basic categories [3], a) destructive process such as destructive oxidation with ozone [4], hydrogen peroxide [5] or manganese oxides [6] and b) recuperative processes such as adsorption into porous solids [7], membrane separation [8] and solvent extraction [9].

In recent years adsorption systems using activated carbon have been widely employed in the purification of water and wastewater, which industries employ to reduce hazardous organic and inorganic wastes in effluents. The content of phenolic compounds in industrial wastewater (about 200-2000 mg /L) is usually higher than the standard limits (mostly less than 0.5 mg L) established for their release into aquatic environment. Therefore, extensive research work has been carried out using activated carbons and resins [10]. Many researchers [11] have shown that activated carbon is an effective adsorbent for organic compounds, especially for phenolic compounds. However, its high initial cost makes it less economically viable as an adsorbent. Taking these criteria into consideration, the search for a low coast and easily available adsorbent has led many investigators to search more economic and efficient techniques using natural and vegetal adsorbents.

The objective of our work is to eliminate phenol by adsorption onto an adsorbent obtained from a local cereal by-product.

2. Material and methods

2.1. Materials:

2.1.1 Adsorbent:

The local cereal by-products were:

- washed;
- Calcined at a temperature of 600C in exclusion of air in an electrical furnace (HEARAEUS D-6450 HANAU/Germany);
- Crushed in a crusher (FRITSCH industry.8 6580 Idar Oberstein);
- Sieved into particule size of 0.1mm, using a sifter (Analysensieb-retsch-5657 HAAN W);
- Finally, the solid material obtained is stored in a desiccator for use.

2.1.2 Phenol:

The solution of phenol was prepared from solid phenol (crystalline form) provided by Cheminova Internacional SA (Spain). The pH of the solution is adjusted with nitric acid HNO3 (0.1N) and caustic soda NaOH (0.1N). Calibration curves have been prepared using sample solutions of 1g/l as recommended in [2], for the reading of all concentrations.

The water used in this study for the preparation of the solutions of phenol was bi distilled using a distiller GFL 2001/4 distillation.

2.2 Experimental protocol:

The samples of solutions are prepared according of the following steps:

- Mixing of 2g of the solid material with a solution volume of 200ml to phenol;

- Agitation at 600 rpm during 120 minutes at a temperature of 20C;
- Filtration of the solution on filters microspores of diameter 0.4mm;
- Measurement of the pH of the filtrate collected;
- Analysis or the filtrate by UV (UV-Visible Spectrophotometer UV 1601.Shimadzu) directly after filtration;
- Determination of the adsorption capacity

Effect of parameters such as the time of contact, the pH, the initial concentration, was studied. In order to obtain the optimum of each parameter, we vary this last, and to leave all the other constant ones.

In order to obtain the isotherms of adsorption, we put in contact 0.5g of solid material with 50ml of the solution at initial concentrations going from 2 to 50mg/l in the first stage of the work then from 2 at 100mg/L in the second and finally from 2 at 500mg/L (speed = 600tr/min, temperature = 20°C). Equilibrium is assumed to have been reached after 120 min and the filtrate collected is analyzed.

3. Results and discussion

3.1 Effect of contacting time

Obtaining the equilibrium time of adsorption is necessary for determining the various constituent points of the isotherms and its nature. Since adsorption is a process of transfer of the pollutant from the liquid phase to the solid phase, time between the two phases is a limiting factor.

The study consists to put in contact, a volume of 200ml of a solution of phenol (20 mg/L) with 2 g of solid material prepared at the laboratory. The mixture is put in agitation at 600tr/min and 20C then we follow the variations of the concentration of the liquid phase with the time. Results obtained for our organic pollutant, which is the phenol are represented on the following figure:

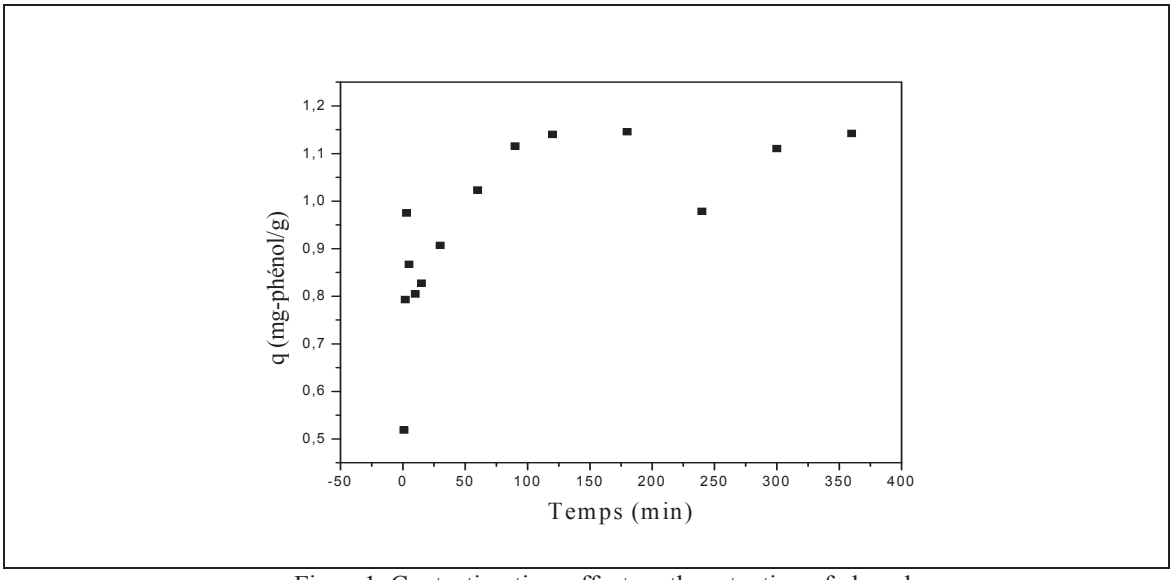


Figure1. Contacting time effect on the retention of phenol
Conditions : C_0=20mg/l, pH5.24, 20.1°C, v=600tr/min, r=10g/l, d<0.1mm

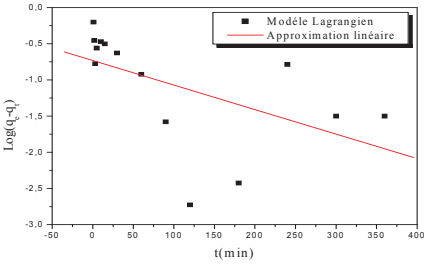
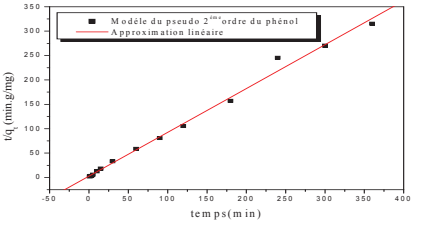
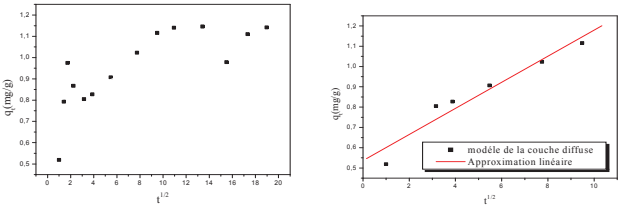
According to the figure represented above we notice that equilibrium is practically reached at the end of 90 minutes. The results obtained show the existence of two phases; the first rapid and the second slow one. This relates to the great availability of the free active sites of the adsorbent at the beginning of the experiment and which becomes weak as one advance in time.

3.2 Kinetic study

Several kinetic models (the model of diffusion on homogeneous surface, the model of the diffusional pores, and the heterogeneous model of diffusion and the model of elkovich) are tested on our experimental results in order to describe the mechanism of the process of adsorption (mass transfer, chemical reaction). The results of the four models are represented on the figures 2.3.4.et 5.

The factors of correlation of the four equations as well as constants the kinetics of each model are represented on the table 2.

Table 1. Kinetic models

Lagrangien's model k_1 : The constant speed for kinetics of the pseudo first order; q_t : capacity of adsorption at the moment t q_e : la capacity of adsorption to equilibrium	
	Figure 2. *of phenol Kinetics of the pseudo first order*
Model of the pseudo second order $\frac{t}{qt} = \frac{1}{K^2 \cdot q_{e2}^2} + \frac{1}{q_{e2}} t$ k_2 : the constant speed for second-order kinetics q_t : capacity of adsorption at the moment t q_e : la capacity of adsorption to equilibrium	
	Figure 3. *Kinetic of the pseudo second order of phenol*
Model of the diffuse layer $q_t = k_{int}\, t^{1/2}$ k_{int} : the constant of the diffusion will intra particle in (mg/g $min^{1/2}$)	
	Figure 4. *Kinetic model of the layer diffuses phenol*

Elovich's model

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$$

α: the rate of initial adsorption in (mg/g min)

β : constant connected to external surface and the energy of activation of the chimiosorption in (g/mg)

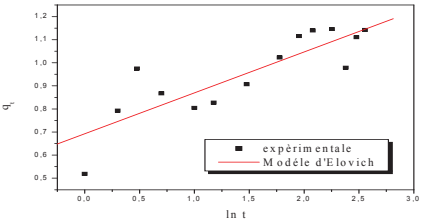


***Figure 5**. Kinetic model of Elkovich of the adsorption of phenol*

Table 2. Constants of the kinetic models of adsorption of the phenol (1st order, 2nd order, the diffuse layer and Elovich

Lagrangien's model	K_1 (min^{-1})	0.007807
	q_e(mg/g)	0.18543
	Factor of correlation R^2	-0,5391
Kinetic Model of the pseudo second order	K_2 (g mg^{-1} min^{-1})	0.5533594
	q_e(mg/g)	1.15129
	Factor of correlation R^2	0.99691
Kinetic Model of the layer diffuses	k_{int}	0,06429
	D (cm^2 /s) ($t_{1/1}$=0.03 r_0^2/D)	1.735 10^{-9}
	Factor of correlation R^2	0,96656
Elovich's model	α	-0.9443
	β	1.4429
	Factor of correlation R^2	0.84754

From this table, we can conclude that the retention of phenol by our support prepared at laboratory (DCC) is better represented by second-order kinetics indicating a chemical reaction, (chimiosorption). But it can be also represented by a diffusion intra particle model

3.3 Effect of the pH

The adsorption of weak electrolyte such as phenol compounds, on the surface of a porous amphoteric solid, such as activated carbon, from aqueous solutions depend, mainly on two important factors. One of them is the degree of dissociation of the electrolyte and the other is the dominant charge on the surface of the solid; Both factors can be qualitatively predicted by the pKa (activity constant) of the weak electrolyte, because at a solution pH lower than the pKa it will remain undissociated [13]. However the second factor is more difficult to ascertain.

The effect of the solution pH on the adsorption capacity of cereal by-product for phenol studied is shown in figures 6, 7 and 8

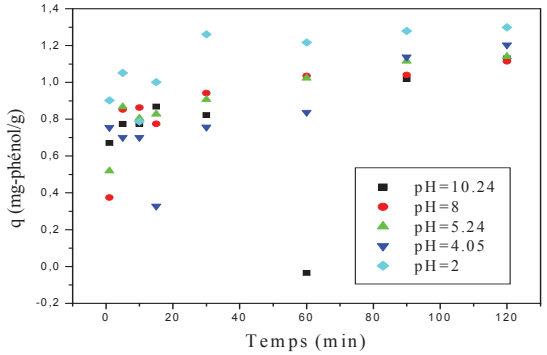


Figure 6. *Effect of pH on retention of phenol*
Conditions : C_0=20mg/l, t=120min, 20°C, v=600tr/min, r=10g/l, d<0.1mm

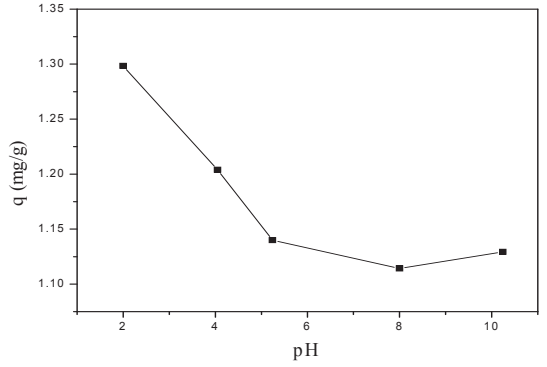


Figure 7. *Influence of pH on maximal capacity of retention of phenol*

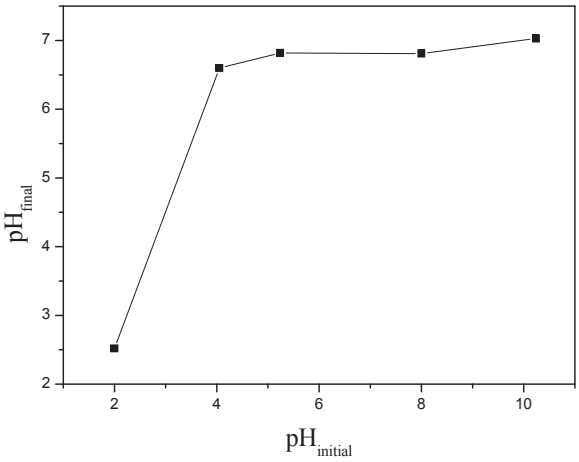


Figure 8. *Variation of finally pH with initially pH*

According to the figures, it appears clearly that the rate of retention of phenol varies with the pH.

At acid pH (pH=2), the output of the retention is relatively high, it is at the maximum. By increasing the pH, the rate of retention decreases gradually. It reaches its minimum at basic pH (pH=8).

When the pH is low there is a release of the ions H^+.The concentration of the hydrogen ions H^+ affects the ionization level of the phenolic adsorbate and the properties of surface of the adsorbent.. This can be explained on the basis of formation of a surface charged and oxides negatively charged on surface with current hydroxylated oxides on surface with the adsorbent [14].

With low values of the pH, the only pair of electrons of the oxygen atom not dissociated. Grouping OH in the benzene cycle coordinates with surface positively charged. This is also confirmed by the report/ratio that an increase in the rate observed as the pH decreases, can be caused by deterioration in the surface of the adsorbent, in particular the variation of its electrokinetic nature as the pH changes. A low pH probably has like consequence a lowering of the negative charge on the surface of the adsorbent, of this fact increasing the adsorption of the adsorbent negatively charged. But with higher values of the pH the dissociated phenolate ion ($C_6H_5O^-$) is pushed back by oxide negatively charged on surface [1I].

The results indicate that the phenol is preferentially adsorbed on the surface of cereal by-product in his molecular form, because at acidic pH values it is not dissociated. The phenol start to dissociate at a pH close to their pKa value, which is 9,96. However, the amount of phenol adsorbed depends also on the surface charge of the solid. At pH values higher than 10, both the external and internal surface are negatively charged and the phenol is also dissociated [11].

The following reactions of surface illustrate the probable behavior of our support.

$$S\text{-}OH + H^+ \leftrightarrow SOH_2^+$$
$$S\text{-}OH + OH^- \leftrightarrow S\text{-}O^- + H_2O$$

Thus the holding capacity of phenol decreases as follows:

pH 2 > pH 4.05 > pH 5.24 > pH 8 > pH 10.24

3.4 Isotherms of adsorption

The adsorption isotherm is the variation the quantity q of compound adsorbed on a solid according to the partial pressure P or of the concentration adsorbable in the fluid in contact, at a constant temperature q= f(P) or q = f(C).

With an aim of determining the type and the nature of the adsorption isotherm of phenol on cereal by-product (DDC).We varied the initial concentration from 2 to 50 mg/L initially then of 2 with 100mg/L and finally of 2 with 500mg/l.The results collected are represented on the three following figures:

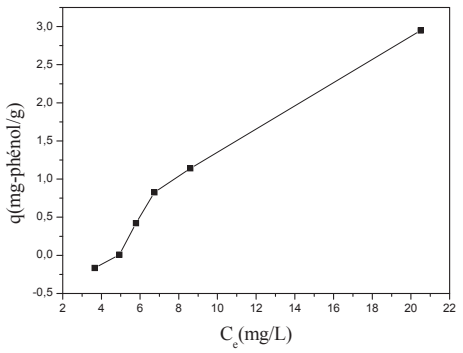


Figure 9. Adsorption isotherm of phenol (C_0=2 à 50mg/L)

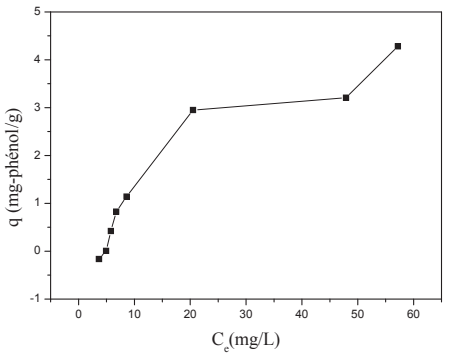


Figure 10. Adsorption isotherm of phenol (C_0=2 à 100mg/L)

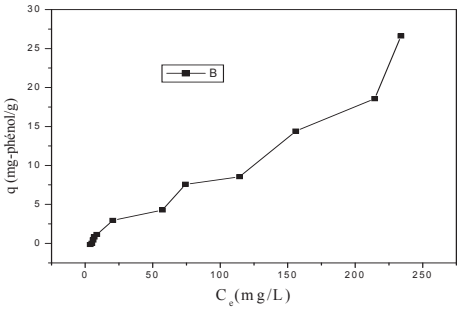


Figure 11. Adsorption isotherm of phenol (C_0=2 à 500mg/L)

According to the figures represented above, we can notice that graphically, the experimental data show an isotherm with multi-layer called isotherm with steps. This particular type of isotherm does not enter the traditional classification of Brunauer, Deming and Teller. LETORT, DUVAL and BONNETAIN were

among the first to describe this isotherm: type VIII called in staircase or with steps. This model presents an abrupt increase in adsorption moving one or more.

The origin of these steps is the formation on the surface of the solid of a structure of adsorbate two-dimensional, liquid if she is not rigorously ordered, or solid if the structure is ordered. The phenomenon of adsorption corresponds then to the condensation of the adsorbate. The concerned interactions are thus mainly not interactions solid-adsorbate as in the models langmuir or BET but interactions `side' adsorbate-adsorbate neglected in the traditional models. This result is in agreement with the study established by M.L. SOTO and A. MOURE in the study of the adsorption of the phenolic compounds on coal.

The existence of several steps corresponds to the existence of several successive two-dimensional phases [full-course 1 on solid], [monocouche2 on monocouche1].

Until now there is not a ideal model which characterizes this type of adsorption on several floors. But with an aim of identifying the mechanism of retention on the first floor (C_0 = 2 to 100 mg/L), and of identifying the isotherm which represents best the adsorption of phenol on the DCC we tested four ideal models on our resulted experimental. Namely Langmuir, Freundlich, BET and the model of Temkin. The calculated parameters are represented on table 3.

Table 4. Parameters of various models of isotherms

	Langmuir	Freundlich	BET	Temkin
Model	$\frac{1}{q}=\frac{1}{b}+\frac{1}{abC}$	$Log\,q = LogK + \frac{1}{n} LogC$	$\frac{C}{q(C_0-C)} = \frac{1}{q_m K} + \frac{K-1}{q_m K}\left[\frac{C}{C_0}\right]$	$q = \frac{RT}{b}\ln A + \frac{RT}{b}\ln C$
R^2	0,5889	0,72916	0,99975	0,99447

According to these resulted we see clearly that the phenomenon of adsorption is represented better by an isotherm with multi-layer (BET). This model gives a factor of correlation of 0.99975. The theoretical value of the capacity at the equilibrium of full-course qm (qm=1.154689 mg/L) coincides with the experimental value which is of 1.1456822 mg/g.

4.Conclusion

This study shows that cereal by-product, an abundant natural material, can be used effectively and efficiently for the removal of phenol from wastewater. The adsorption of phenol reached equilibrium in 120 minutes. The results indicate that adsorption capacity of the sorbent was considerably affected by initial phenol concentration, and pH.

From linear regressions testing the kinetics of retention, it can be concluded that the adsorption of phenol by our natural adsorbent (DCC) is much better represented by a second order kinetic and can be seen clearly on the values of R ; -0.5391 for the first test and 0.99691 for the second. This kinetic is controlled by external mass transfert followed by intraparticle diffusion mass transfert.

The experimental results show an isotherm of type VIII according to the classification of Brunauer, Emmet and Teller. This is called multilayer isotherm or isothermal steps. Each step is a BET (Brunauer, Deming and Teller) This is confirmed by the results of the application of that model on the first level of the curve (2 to 100 mg / L).

We found that with a concentration of 20mg / l and a temperature of 20 ° C, particle size less than 0.1mm, a mixing velocity of 600tr/min a report de0.5g adsorbent / 50ml of the solution (10g / l), pH ≈ 3, the efficiency of retention reached 70%

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